

# A Computational Study of Thirteen-atom Ar-Kr Cluster Heat Capacities

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## Abstract

Heat capacity curves as functions of temperature were calculated using Monte Carlo methods for the series of  $\text{Ar}_{13-n}\text{Kr}_n$  clusters ( $0 \leq n \leq 13$ ). The clusters were modeled classically using pairwise additive Lennard-Jones potentials. J-walking (or jump-walking) was used to overcome convergence difficulties due to quasiergodicity present in the solid-liquid transition regions, as well as in the very low temperature regions where heat capacity anomalies arising from permutational isomers were observed. Substantial discrepancies between the J-walking results and the results obtained using standard Metropolis Monte Carlo methods were found. Results obtained using the atom-exchange method, another Monte Carlo variant designed for multi-component systems, were mostly similar to the J-walker results. Quench studies were also done to investigate the clusters' potential energy surfaces; in each case, the lowest energy isomer had an icosahedral-like symmetry typical of homogeneous thirteen-atom rare gas clusters, with an Ar atom being the central atom.

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## I. INTRODUCTION

The study of clusters has shown these systems to exhibit a surprisingly rich diversity of interesting phenomena. It has helped provide much insight into the transition from finite to bulk behavior, since many of the physical properties of bulk systems are highly modified in clusters because of their much greater fraction of surface atoms. Although most studies have dealt with homogeneous clusters, heterogeneous clusters have been increasingly the subjects of both experimental<sup>1-8</sup> and theoretical<sup>9-23</sup> investigations. Most of these studies have concentrated on bimetallic clusters, in large part because of the roles they play in catalysis. Heterogeneous clusters are also important theoretically, since the cluster composition provides another variable that can be exploited to better understand the transition from microscopic to macroscopic behavior. Much of the intriguing behavior of homogeneous clusters, such as their varied melting behavior<sup>24-37</sup> and the appearance of “magic number” effects in many cluster properties as functions of aggregate cluster size,<sup>38-41</sup> is also observed in heterogeneous clusters, but this behavior can be strongly dependent on the cluster composition.

It is the desire to better understand the role cluster composition plays in the thermodynamic properties of heterogeneous clusters that has motivated my present work, and so I have used binary rare gas clusters as my subject. These systems can be adequately described by a simple pairwise additive Lennard-Jones potential, unlike bimetallic clusters, which require more complicated (and computationally expensive) potentials for proper treatment.<sup>9</sup> I have also chosen Ar and Kr as the two components because their atomic sizes are similar enough that most of the physical properties of the homogeneous clusters are not drastically altered in going to binary clusters of similar aggregate size; a related study of Ne-Ar clusters, where the atomic sizes are sufficiently dissimilar that the physical behavior of the binary clusters differs radically from that of their homogeneous counterparts, is nearing completion and will be submitted for publication shortly.

I have also limited the current study to thirteen-atom clusters. Thirteen-atom

homogeneous<sup>23–30,41–43</sup> and heterogeneous<sup>9–15</sup> clusters have been the subject of many studies. The homogeneous clusters exhibit “magic number” effects for many of their properties that are a manifestation of their compact icosahedral ground state configuration. Because Ar and Kr have similar sizes (the Ar radius is about 11% smaller than the Kr radius), thirteen-atom Ar-Kr clusters also have icosahedral-like lowest-energy configurations that are only slightly distorted; Tsai, Abraham and Pound<sup>14</sup> found the lowest-energy configuration of Ar<sub>7</sub>Kr<sub>6</sub> to be icosahedral-like, and Lopez and Freeman<sup>15</sup> found the ground state configuration of Pd<sub>6</sub>Ni<sub>7</sub> clusters to be icosahedral-like as well (the Ni-Pd radius ratio is very similar to the Ar-Kr radius ratio). This size similarity then leads to two different categories of isomers: topological isomers based on geometric structures that are similar to those of their homogeneous counterparts, and permutational isomers, which are based on the various rearrangements of the different component atoms within a topological form. While homogeneous clusters have only topological isomers, heterogeneous clusters can have several permutational isomers associated with each topological form, depending on the cluster composition. For Pd<sub>6</sub>Ni<sub>7</sub>, Lopez and Freeman found that neither changing the potential model nor the Pd-Ni interaction strength had any effect on the topological form of the ground state isomer (which was always icosahedral-like), but did strongly effect which of the permutational isomers had the lowest energy, with the segregated isomer being lowest for lower Pd-Ni interaction strengths, and the mixed isomer being lowest for higher interaction strengths. Similar results were obtained by López, Marcos and Alonso<sup>9</sup> in their study of thirteen and fourteen-atom Cu-Au clusters.

One of the more sensitive cluster properties is the heat capacity, which has been useful in elucidating the nature of cluster solid-liquid “phase” transitions.<sup>15,25–27,41–46</sup> Heat capacity curves as functions of temperature for homogeneous thirteen-atom clusters are characterized by a very large peak in the solid-liquid transition region that is a consequence of the large energy gap between the ground state icosahedral isomer and the higher energy non-icosahedral isomers.<sup>25–27,41–43</sup> Lopez and Freeman<sup>15</sup> showed that the heat capacity curve for Pd<sub>6</sub>Ni<sub>7</sub> is quite similar to the homogeneous case, which is largely due to the two having similar topo-

logical isomers. However, they also observed the effects of the permutational isomers, made manifest as an additional, very small, heat capacity peak occurring at very low temperatures. This feature, arising from the low-energy icosahedral-like isomers is reminiscent of order-disorder transitions known to occur in some bulk alloy materials.

Cluster heat capacities are notoriously difficult to calculate accurately using simulation methods because of poor convergence. This is due to quasiergodicity, or the incomplete sampling of configuration space, which arises in systems characterized by well separated regions that are linked by very low transition probabilities because of bottlenecks in the configuration space. Thus the sampling is effectively confined to only a small subset of the important regions.<sup>48</sup> In the past, this has necessitated the use of extremely long simulations to ensure proper sampling, and it has only been recently that advances in computer technology have made accurate heat capacity calculations from simulations feasible. In addition, new methods have been developed that substantially reduce quasiergodicity and dramatically increase convergence in Monte Carlo simulations. These methods are characterized by their use of large scale movements, or jumps, of the random walker to various regions of configuration space and so are denoted “J-walking” or “jump-walking.”<sup>26</sup> J-walking has been used successfully in several studies,<sup>27,41,44–47</sup> including the Lopez and Freeman work,<sup>15</sup> where it not only worked well in the  $\text{Pd}_6\text{Ni}_7$  solid-liquid transition region, but also in the very low temperature mixing-anomaly region; the mixing-anomaly peak was not obtained using the usual Metropolis method,<sup>49</sup> but was seen only when J-walking was used. J-walking was used in this study as well.

I begin in Section II with a description of the various computational methods I used, including a brief discussion of my implementation of the J-walking method for binary clusters. Section III first examines the structural properties of the thirteen-atom Ar-Kr clusters, then discusses the results obtained using J-walking for the heat capacities and potential energies as functions of temperature. These are compared to the results obtained from similar calculations done using the standard Metropolis method, and to the results obtained from a modified Metropolis scheme incorporating an atom-exchange algorithm.<sup>14</sup> While atom-

exchange techniques provided substantial improvement over the unaided Metropolis method for the heat capacities at very low temperatures, they were still unable to overcome the quasiergodicity difficulties nearly as well as the J-walking method. The results of quench studies are also discussed. Finally, in Section IV, I summarize my findings and discuss some of the insights provided by the binary cluster results.

## II. COMPUTATIONAL METHOD

Monte Carlo simulations were run for all clusters in the series  $\text{Ar}_{13-n}\text{Kr}_n$  with  $0 \leq n \leq 13$ . The clusters were modeled by the usual pairwise additive Lennard-Jones potential,

$$V = \sum_{i < j} V_{LJ}(r_{ij}),$$

$$V_{LJ}(r_{ij}) = 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right]. \quad (1)$$

Table I lists the Lennard-Jones parameters.<sup>50</sup> The Ar-Kr interaction parameters were determined from the usual Lorentz-Berthelot mixing rules;<sup>51</sup> the reader is referred to the work by Lopez and Freeman concerning the effects of using generalized mixing rules for  $\text{Pd}_6\text{Ni}_7$ .<sup>15</sup> The classical internal energy and heat capacity were calculated by the usual expressions for an  $N$ -atom cluster,

$$\langle U^* \rangle = \frac{3NT^*}{2} + \langle V^* \rangle, \quad (2)$$

$$\langle C_V^* \rangle = \frac{3N}{2} + \frac{\langle (V^*)^2 \rangle - \langle V^* \rangle^2}{(T^*)^2}. \quad (3)$$

The reduced units are in terms of the Ar-Ar interaction, with  $U^* = U/\epsilon_{\text{Ar-Ar}}$ ,  $V^* = V/\epsilon_{\text{Ar-Ar}}$ ,  $C_V^* = C_V/k_B$ , and  $T^* = k_B T/\epsilon_{\text{Ar-Ar}}$ .

Because of their finite vapor pressure, small clusters are known to become unstable at sufficiently high temperatures.<sup>43,52</sup> For clusters modeled with the Lennard-Jones potential under free volume conditions, the average energy vanishes in the limit of infinitely long walks. Consequently, the choice of boundary conditions can greatly effect some cluster properties

at higher temperatures.<sup>31</sup> I have followed Lee, Barker and Abraham<sup>53</sup> and have confined the clusters by a perfectly reflecting constraining potential of radius  $R_c$  centered on the cluster’s center of mass. To maintain a common set of boundary conditions throughout the survey, the constraining radius was identical for all the clusters studied, with  $R_c = 3\sigma_{\text{Kr-Kr}}$ . As will be described later, the use of a constraining sphere for the simulation of binary clusters led to some computational difficulties that required special handling.

### A. J-Walking

Standard Monte Carlo simulations of clusters based on the sampling algorithm proposed by Metropolis *et al.*<sup>49</sup> are known to suffer from systematic errors due to quasiergodicity,<sup>48</sup> the non-ergodic sampling that typically arises with configuration spaces that are comprised of several regions separated by large barriers. For certain temperature domains, this can lead to bottlenecks that effectively confine the sampling to only some of the regions, resulting in large errors.<sup>51</sup> These systematic errors are purely a consequence of the practical limitations placed on the walk lengths, since, for sufficiently long walks, the random walker overcomes the bottlenecks often enough to provide ergodic sampling. The required walk length depends on the temperature; for higher temperatures, the random walker’s stepsizes are large enough that movement between the various regions occurs frequently and so shorter walk lengths are adequate. As the temperature decreases, so does the probability of moving between regions, thus requiring that the walk lengths be increased. The potential hypersurfaces for clusters typically have deep wells corresponding to very stable, compact isomers that are separated from one another by large barriers. For high temperatures corresponding to the cluster’s “liquid” region where unhindered isomerization occurs, the random walker has full access to all of configuration space. However, for temperatures in the solid-liquid transition region, a dichotomy of time scales characterizes the random walks, producing rapid movement within the isomeric regions, but only very slow movement between them.

J-walking addresses the problem of quasiergodicity by coupling the usual small-scale

Metropolis moves to occasional large-scale jumps that move the random walker to the different regions of configuration space in a representative manner.<sup>26</sup> In the following paragraphs, I give a brief summary of the method and describe some of the aspects that were important in implementing the method for heterogeneous clusters; the reader is referred to the original papers for a more complete description of the general algorithms.<sup>26,46</sup>

The large-scale jumps are governed by Boltzmann distributions generated at higher temperatures where the sampling is ergodic. There are two complementary implementations for generating the classical J-walker Boltzmann distributions. The first runs the high temperature walker (J-walker) in tandem with the low temperature walker, with the low temperature walker occasionally attempting jumps to the current J-walker position simply by using the current J-walker coordinates as its trial position. The high computational cost of this implementation limits its practical use to parallel computers. In the second implementation, the J-walker is run beforehand and the configurations generated during the walk are stored periodically in an external array. Subsequent jump attempts are made by accessing the stored configurations via randomly generated indices. This implementation has only a modest computational overhead (mostly the time required to generate the distributions), but requires very large storage facilities for handling the distribution arrays. Because fast workstations (and even personal computers now) having tens of Mb of RAM and Gb of disk storage are affordable and quite common, while access to parallel computers is still much more limited, this implementation remains the method of choice and was the one used for all the J-walking calculations reported in this study.<sup>54</sup> The reader is referred to a recent study of ammonium chloride clusters by Matro, Freeman and Topper for a description of a parallel J-walking implementation that combined the tandem-walker and external-file methods.<sup>44</sup>

For physically realistic systems such as clusters, the Boltzmann distributions are generally too narrow for a single distribution to span the entire temperature domain, and so the distributions have to be generated in stages. For each cluster studied, an initial J-walker distribution was generated from a long Metropolis walk at a temperature high enough for the sampling to be ergodic. This distribution was then used for J-walking runs to obtain

averages of the potential energy and the heat capacity for a series of lower temperatures. The J-walker distribution's width placed practical limitations on the effective temperature range for the subsequent J-walking simulations. When the temperature difference between the distribution and the low temperature walker became too large, very few attempted jumps were accepted since the J-walker configurations likely to be accepted were in the low energy tail of the distribution. Thus, at the temperature where the jump acceptance became too small,<sup>55</sup> a new distribution was generated from the previous one, using J-walking to ensure it was ergodic as well. This distribution was then used to obtain data for the next lower temperature range, and then to generate the next lower temperature J-walker distribution, and so on, until the entire temperature domain was spanned. The distributions used in this study each consisted of at least  $10^6$  configurations. Because the configurations generated during Metropolis walks are highly correlated, they were stored in a periodic fashion. The higher temperature distributions were the widest, and contained the greatest variety of configurations; these were generated by storing configurations every hundred passes. For the narrower lower temperature distributions, the sampling was reduced to every fifty or twenty-five passes, and for the very narrow distributions for the low temperatures corresponding to the solid region, a sampling of every ten passes was sufficient.

The J-walker calculations were done in a manner mostly analogous to a previous J-walker study I did on a series of homogeneous clusters ranging in size from four to twenty-four atoms.<sup>41</sup> In that study, a larger constraining radius ( $R_c = 4\sigma$ ) was chosen to freely accommodate the larger clusters, and the initial J-walker distributions were all generated at higher temperatures corresponding to the cluster dissociation region. This was done to eliminate small effects of quasi-ergodicity occurring in the liquid-dissociation transition region for some of the larger clusters. Preliminary calculations indicated that using such high initial temperatures for small binary clusters resulted in problems with the cluster constraining potential due to the simulations not using center of mass coordinates. For such simulations, the center of mass (and thus the cluster as a whole) will drift during the course of the walk, requiring that the center of mass coordinates be updated for each

accepted move. This can be easily done, and the computational overhead is quite low. In this scheme, attempted Metropolis moves are checked for constraining potential violations by calculating the new center of mass consistent with the trial move and checking if the distance to the new center of mass is greater than the constraining radius  $R_c$ . If it is, the attempted move is rejected outright, otherwise, the usual Metropolis criterion is used to determine whether the move is accepted or not. While such a scheme guarantees that the trial atom is never moved outside the constraining potential, it does not guarantee that an accepted Metropolis move does not leave one of the other cluster atoms outside the constraining potential when the move is accepted and the center of mass updated. Such an orphaned atom can then drift away from the rest of the cluster, effecting the results for the remainder of the Metropolis simulation. Although this is a rare occurrence, it can become a significant problem at very high temperatures where the cluster is completely dissociated (thus physically corresponding to a highly compressed gas confined to a small spherical cavity) and there is greater likelihood of atoms being near the constraining surface. The problem is also worse for smaller clusters since these can have larger changes in the center of mass when moves are accepted. Heterogeneous cluster simulations are especially prone to such constraining sphere violations since the interactions between the different components can be quite disparate, leading to the dissociation of one component at temperatures where the other components remain intact.

The constraining potential violations are not a problem for J-walking simulations, provided that the J-walker distributions are free of such violating configurations. This is because a J-walker “walk” is really a series of short “excursions,” each starting from the J-walker configuration last accepted. Thus, should a Metropolis move ever result in an atom being left outside the constraining potential, the next accepted jump would restore the configuration to a valid one. This does require that much care be exercised in ensuring that proper J-walker distributions have been generated from the initial high temperature Metropolis walks. So, for each cluster studied, the initial J-walker distributions were generated at temperatures in the cluster liquid region (from 44 K for  $\text{Ar}_{12}\text{Kr}$  to 58 K for  $\text{ArKr}_{12}$ ), well

below the cluster dissociation region. Even at these temperatures, single atom dissociations occurred frequently enough that a few constraining potential violations occurred. Sampled configurations for these high temperatures were stored in the J-walker distribution files only every hundred passes, and since checking every atom for possible constraining potential violations for every accepted move is computationally expensive, and considering that the frequency of violations was very low, I instead found it preferable to simply generate extra configurations and then check every configuration in the distribution, discarding any violating configurations (typically less than 0.1% of the configurations stored).

Correlations in the J-walker distributions were further reduced by writing the distribution files in a parallel fashion. All output distribution files were opened at the start of the program and configurations were written to each in turn, rather than writing to each file sequentially, one at a time. Thus, each distribution file contained configurations sampled from the entire run. Although this resulted in highly fragmented files, which could have greatly increased the time required to later read a distribution into memory, this did not turn out to be a problem because as each distribution file was subsequently checked for constraining potential violations, the valid configurations were written to the disk sequentially.

Preliminary calculations also indicated another important difference between the binary cluster simulations and the homogeneous cluster calculations done previously.<sup>41</sup> In those calculations, comparison of the J-walking heat capacity results for a given cluster size that were obtained from different, independently generated distributions were in agreement with one another, implying that the distributions were sufficiently representative and thus any systematic errors were negligible. Those results were obtained from averages collected from  $10^7$  passes for each temperature. For the binary clusters however, there were small differences between the J-walking heat capacity results obtained from different, independently generated sets of distributions, indicating that small systematic errors were present in the J-walking heat capacity data that were larger than the uncertainties associated with random fluctuations obtained with  $10^7$  passes. This was most likely a consequence of the large increase in the number of isomers in the binary cluster case because of the extra permuta-

tional isomers, which made obtaining representative samples that much more difficult. To ensure there were no significant systematic errors in the binary cluster heat capacity curves, I therefore ran five separate J-walking trials, with each trial sampling from its own unique set of J-walker distributions. The results for the five separate trials were then combined and averaged, with the standard deviation taken as an estimate of the uncertainty. For each trial, the total walk length was set to  $10^6$  passes of data accumulation, so that the total computational time was not much longer than that for a single run of  $10^7$  passes. Fig. 1 shows the results for  $\text{Ar}_8\text{Kr}_5$ . As can be seen in the plot, the noise level in each curve is about the same magnitude as the differences between the curves, indicating that these walk lengths were sufficiently long for the desired level of accuracy. Also shown are the results obtained for two similar J-walking trials, each sampling from a set of distributions initially generated at  $T = 70$  K, a temperature corresponding to the high temperature side of the cluster dissociation peak. Systematic errors are clearly evident in these curves. Not only do they differ substantially from the five J-walking curves generated from the initially lower temperature J-walker distributions (especially at the very low temperatures in the mixing-anomaly region), they do not even agree between themselves, showing large differences in the solid-liquid transition region.

## B. Standard Metropolis

Since J-walking is a relatively new method, and experience with it is still being obtained, I also ran standard Metropolis simulations for each cluster. These provided a check of the J-walking results for those temperature regions where quasiergodicity in the Metropolis runs was not a problem, as well as revealing trends in the systematic errors arising from quasiergodicity in the Metropolis runs as functions of cluster composition. Temperature scans were generated with a mesh size of  $\Delta T = 0.1$  or  $0.2$  K for very low temperatures, and  $\Delta T = 0.5$  K for higher temperatures. For each temperature, simulations consisted of  $10^5$  warmup passes, followed by  $10^7$  passes with data accumulation. The scans were started at

the lowest temperature using the global minimum configuration and were continued past the cluster melting region, with the final configuration for each temperature used as the initial configuration for each subsequent temperature. For almost all of the clusters examined, the Metropolis and J-walking heat capacity results agreed qualitatively throughout, except for very low temperatures where small peaks associated with mixing anomalies were absent in the Metropolis curves. They agreed quantitatively over much of the temperature ranges as well, with the largest discrepancies occurring mostly in the solid-liquid transition region effecting the peak height and location. Interestingly, the agreement was worse for those clusters having a higher proportion of Kr. Fig. 1 also shows the Metropolis results for  $\text{Ar}_8\text{Kr}_5$ . As can be seen, substantial discrepancies due to quasiergodicity are evident in the solid-liquid transition region, and the low-temperature mixing-anomaly peak is completely absent. Lopez and Freeman<sup>15</sup> obtained similar results in their study of  $\text{Pd}_6\text{Ni}_7$  clusters — J-walking results showed a small mixing-anomaly peak occurring at low temperatures that was absent in the Metropolis results. The open circles in the plot represent Metropolis results obtained using  $10^8$  total passes. These are in agreement with the J-walker results obtained from distributions initially generated at  $T = 52$  K, verifying that the J-walker distributions were free of systematic errors, as well as showing that these Metropolis walks were sufficiently long to overcome quasiergodicity in the solid-liquid transition region.

### C. Atom Exchange Method

The inadequacy of the standard Metropolis algorithm for simulating heterogeneous clusters at very low temperatures has been noted previously. Tsai, Abraham, and Pound<sup>14</sup> developed a simple but effective strategy to help overcome these limitations by incorporating an atom exchange scheme in their Metropolis algorithm. The method enhances the mixing of clusters by occasionally attempting an exchange move where one of the atoms of one component is swapped with one of the atoms of another component. The move is either accepted or rejected according to the usual Boltzmann-weighted criterion. To help resolve

the discrepancies occurring between the standard Metropolis and J-walking methods, I ran atom-exchange simulations for all temperature regions where significant discrepancies were found. These were done in a manner similar to the standard Metropolis runs described previously, with an atom-exchange move between randomly selected Ar and Kr atoms attempted once after every pass of standard Metropolis moves. The results for  $\text{Ar}_8\text{Kr}_5$  can also be seen in Fig. 1. The atom-exchange results are a substantial improvement over the standard Metropolis results in the low temperature region, but are only in qualitative agreement with the J-walker results, showing a mixing-anomaly peak that is much smaller than the J-walker peak and occurring at a higher temperature. Nonetheless, the atom-exchange results lend further validity to the J-walker results and demonstrate that the mixing-anomaly peak is not a spurious artifact of J-walking.

#### D. Quench studies

In their study of the general cluster morphology of binary clusters, Clark *et al.*<sup>17</sup> conveniently characterized the general Lennard-Jones potential parameter space for components A and B in terms of  $\alpha = \epsilon_{AB}/\epsilon_{AA}$ ,  $\beta = \epsilon_{BB}/\epsilon_{AA}$ ,  $\Gamma = \sigma_{AB}/\sigma_{AA}$ , and  $\Delta = \sigma_{BB}/\sigma_{AA}$ . These parameters express the relative interaction strengths and particle sizes for the cluster. Using the Lorentz-Berthelot mixing rules reduces the parameter space dimensionality, with  $\alpha = \sqrt{\beta}$  and  $\Gamma = \frac{1}{2}(1 + \Delta)$ , thus restricting the cluster morphology to regions in the cluster “phase” diagram corresponding to roughly spherical shapes with varying degrees of intermixing between the components, rather than elongated shapes with the two components mostly segregated at either end. Using the values listed for Ar and Kr in Table I, these parameters become  $\alpha = 0.8533$ ,  $\beta = 0.7280$ ,  $\Gamma = 0.9449$  and  $\Delta = 0.8897$ . For medium sized clusters (about 50 to 250 particles) having equal numbers of Ar and Kr atoms at temperatures in the liquid regime, these values of  $\alpha$  and  $\beta$  would correspond to systems mostly consisting of a Kr core surrounded by Ar atoms if the atomic sizes were equal ( $\Gamma = \Delta = 1$ ), but the values of  $\Gamma$  and  $\Delta$  would correspond to a system mostly consisting of an Ar core coated by

Kr atoms if the interatomic interactions were equal ( $\alpha = \beta = 1$ ). Clusters in the liquid regime are sufficiently distended that small size differences between the atoms have only a minor effect, but at the lower temperatures corresponding to the cluster solid region, even small size differences can have a large influence on cluster structure as packing effects become important. Thus there are competitions between the intermolecular forces and atomic sizes that determine the structural properties of binary clusters at various temperatures, and ultimately their dynamical properties. For example, in their study of 55-atom Ar-Kr clusters, Tsai, Abraham and Pound<sup>14</sup> described the competition between the Kr size that was a driving force for its segregation to the surface, and its stronger bond strength that tended to keep it in the interior. For both  $\text{Ar}_{36}\text{Kr}_{19}$  and  $\text{Ar}_{19}\text{Kr}_{36}$ , the Kr atoms tended to reside in the inner shells, while the Ar atoms tended to segregate to the surface, although the central atom in each case was an Ar atom.

At the lower temperatures associated with the cluster solid-liquid transition regions, the competition between the intermolecular forces and atomic sizes effects which of the multitude of isomeric structures will play dominant roles in the cluster's behavior. Thus, information concerning the relative populations of the lower energy isomers encountered during a simulation at a given temperature can offer much insight into the nature of cluster dynamics.<sup>56,57</sup> The relative frequencies of occurrence for each isomer can be obtained from quench studies done during the simulation, where the assumption is that the distribution of minima found in the quenches indicates the likelihood of the system being associated with a particular isomer. That is, the distributions are a reflection of the relative phase volume of each catchment basin.<sup>58</sup> To obtain further insight into the role cluster structure plays, I also performed quench studies on each of the clusters simulated. Steepest-descent quenches<sup>56</sup> were performed periodically on each cluster during one of its five J-walker trials to monitor the relative frequency of occurrence for the lower energy isomers as functions of temperature. For each temperature, quenches were undertaken every 1000 passes, providing 1000 quenched configurations for subsequent analysis. In each case, quench trajectories were run until the relative energy difference converged to within  $10^{-7}$ .

Having a complete listing of all the stable isomers for a given cluster would also be a valuable source of information. Unfortunately, the local minima comprising a typical cluster potential hypersurface are far too numerous to be completely catalogued in any practical manner. However, a reasonably complete listing can be easily obtained from the J-walker distributions. Since the distributions generated at a given temperature contain representative samples of a cluster’s configuration space, a crude, but nonetheless effective, way to identify cluster isomers is to simply quench a sufficient number of the configurations stored in the distributions, saving them in an external file indexed by their energy, and then removing the duplicate configurations. This was done for all the clusters examined in this study. In each case, the configurations in one of the J-walker distribution files generated at the initial J-walker temperature were quenched and analyzed, and all the unique configurations saved to a file. Then the configurations in the next lower temperature distribution were quenched, and the unique configurations added to the file. This was continued until no new configurations were found (this occurred typically with distributions in the temperature range 20 to 30 K). To obtain the highest energy isomers, additional distributions were generated from Metropolis walks at high temperatures in the cluster dissociation region (ranging from 60 to 75 K) and quenched. Again, each configuration was quenched until the relative energy difference converged to within  $10^{-7}$ ; the final composite file of unique isomers was then further refined by running another set trajectories until the relative energy difference converged to within  $10^{-12}$ .

The efficacy of this method was checked by comparing the results obtained for a homogeneous thirteen-atom cluster with those reported in the literature. Hoare and McInnes<sup>59</sup> identified 988 unique isomers for thirteen-atom Lennard-Jones clusters in an extensive study of cluster morphology based on seeding methods. Tsai and Jordan<sup>60</sup> identified 1328 isomers using eigenmode methods, ranging in reduced energy from  $-44.3268$  to  $-35.0706$ . I was able to identify 1167 isomers over the same range by quenching the J-walker distribution configurations. The shortfall is most likely due to my having missed some of the higher energy isomers rather than to having missed lower energy isomers, since the higher energy

isomers are present predominately only in the highest temperature distributions and thus are more easily missed. The lowest energy isomers form an increasing fraction of the lower temperature J-walker distributions and so are encountered frequently enough as the temperature is decreased that it is likely they were all found; all of the twenty lowest energy isomers listed in Ref. 60 were found in the quenched J-walking distributions. Because it is the lower energy isomers that dominate cluster behavior in the solid-liquid transition region, and because I am primarily interested in characterizing cluster solid-liquid transition behavior rather than obtaining a complete listing of the cluster isomers, the list of isomers obtained from J-walker distribution quenches was sufficient for my purposes.

More troubling was that some of the quenched configurations were not local minima, but corresponded to metastable states. Fig. 2 shows the ten lowest isomers obtained for  $\text{Ar}_{13}$  from the J-walker quenches. Two of these were metastable and would eventually relax to a lower energy configuration when repeatedly quenched again with larger stepsizes. The  $-41.55520$  configuration is in fact the lowest energy first-order saddle point found by Tsai and Jordan (none of the other first-order saddle points listed in Ref. 60 were among the J-walker distribution quenched configurations, though). To ensure that no metastable configurations were among the lowest energy binary cluster configurations, the lowest thirty quenched configurations for each cluster were visually inspected. None were found.

### III. RESULTS AND DISCUSSION

#### A. Structural properties

The small size difference between the Ar and Kr atoms suggests that binary Ar-Kr clusters basically have topological configurations similar to their homogeneous counterparts, but with many additional permutational isomers arising from the different arrangements of the Ar and Kr atoms within each type of topological form. This was indeed the case, as can be seen in Fig. 3, which shows the thirteen lowest energy isomers for each of the clusters; their

energies are listed in Table II. These isomers were obtained from quenches of J-walker distribution configurations and are all readily recognizable as variations of the four most stable thirteen-atom homogeneous cluster configurations depicted in Fig. 2, with the ground state in each case being icosahedral-like. For those clusters having several permutational isomers, the segregated isomers have lower energies than the mixed isomers. This is consistent with the results Lopez and Freeman<sup>15</sup> obtained for  $\text{Pd}_6\text{Ni}_7$ , where the lowest energy isomer was also completely segregated (this behavior depended very strongly on the combining rules, though; increasing the value of  $\epsilon_{\text{Pd-Ni}}$  by as little as 2% above the Berthelot-Lorentz rule led to the mixed isomer having the lowest energy).

Given the very large energy difference between the ground state icosahedron and the next three lowest isomers for the homogeneous cluster ( $\Delta E_1 = E_1 - E_0 = 2.85482$  compared to  $\Delta E_2 = E_2 - E_1 = 0.02738$  and  $\Delta E_3 = 0.0502$ ), one might expect that the binary cluster isomers would likewise form widely spaced groupings, with all the icosahedral-like permutations in the lowest energy grouping, followed by all the permutational isomers corresponding to the topological forms having a truncated icosahedral core with a lone displaced atom, and then all the permutational isomers of all the other topological forms. The expected ordering of the low-lying isomers was seen for those clusters consisting mostly of Kr atoms, but not for the Ar-dominant clusters. For  $\text{Ar}_{12}\text{Kr}$ , the other icosahedral-like configuration having the Kr atom as the central atom was not among the lowest thirteen isomers (it was actually the 27th lowest isomer found, with an energy of  $-42.05315$ ). Likewise for  $\text{Ar}_{11}\text{Kr}_2$ , the Kr-core icosahedral-like configuration was much higher in energy (ranking 99th with an energy of  $-43.56749$ ). In each case, the lowest energy isomers all had an Ar atom as the central atom. Although Ar and Kr atoms are sufficiently similar in size that the icosahedral-like configurations dominated the lowest energy isomers, the size difference is large enough that the energy gain obtained by having a Kr core atom (thereby increasing the number of stronger Ar-Kr interactions) is more than offset by the energy lost with the increased separation of the Ar atoms from one another as they are wrapped around the larger Kr core. As the fraction of Kr atoms increases, this energy difference decreases, and the Kr-core icosahedral-like

isomers became energetically favorable relative to the non-icosahedral isomers.

The trends in the minimum energy distributions as the fraction of Kr atoms increases are shown in Fig. 4, which depicts the energy spectrum for each cluster’s local minima relative to its global minimum. Again, the energies were all obtained from J-walker distribution quenches. The plots have been arranged so that complementary clusters ( $\text{Ar}_{13-n}\text{Kr}_n$  and  $\text{Ar}_n\text{Kr}_{13-n}$ ) appear in the same column. The densities of the energetically distinct local minima increase as the number of permutational isomers increases, and for the non-icosahedral isomers become so great that most of the individual levels cannot be distinguished in the plots. Those clusters having a greater fraction of Ar atoms have an energy spectrum similar to that of  $\text{Ar}_{13}$ , which is dominated by its very large energy gap between the icosahedral ground state and the three closely spaced truncated icosahedral isomers with their lone displaced atom (and to a lesser extent by a substantial energy gap between these three isomers and the subsequent higher energy non-icosahedral isomers). As the fraction of Kr atoms in the cluster increases from  $\text{Ar}_{12}\text{Kr}$  to  $\text{Ar}_7\text{Kr}_6$ , the number of Ar-core icosahedral-like permutational isomers increases, forming a small group of closely spaced low lying energies. Similarly, the number of truncated icosahedral and non-icosahedral permutations increases rapidly. The energy spread for the different permutational isomers is large enough that the higher energy gaps seen in the  $\text{Ar}_{13}$  spectrum become increasingly filled, so that by  $\text{Ar}_{10}\text{Kr}_3$  the spectrum consists mostly of a small group of Ar-core icosahedral-like isomers well separated from a large “band” of truncated icosahedral and non-icosahedral isomers; the gap between the two remains relatively constant as the Kr fraction increases to  $\text{Ar}_7\text{Kr}_6$ .

The small triangles in the plots each indicate the lowest energy icosahedral-like isomer found having a Kr central atom. As can be seen in the plots, the energy difference between these isomers and the ground state Ar-core isomers decreases steadily as the Kr fraction increases from  $\text{Ar}_{12}\text{Kr}$ , where the isomer energy is much higher than even that of some of the non-icosahedral isomers, to  $\text{ArKr}_{12}$ , where the energy lies much closer to the ground state than to the next highest energy isomer. By  $\text{Ar}_7\text{Kr}_6$ , the Kr-core icosahedral-like isomers form another small group that lies intermediate between the low energy Ar-core icosahedral-like

group and the higher energy truncated icosahedral and non-icosahedral band. As a consequence, the energy spectra for the  $\text{ArKr}_{12}$  to  $\text{Ar}_6\text{Kr}_7$  sequence of clusters are qualitatively different than those of their  $\text{Ar}_{12}\text{Kr}$  to  $\text{Ar}_7\text{Kr}_6$  counterparts. As will be seen later, this qualitative difference carries over to the heat capacity curves as well.

The decrease in the energy difference between the Kr-core and the Ar-core icosahedral-like isomers as the Kr fraction increases appears to be nearly linear across the series. This is a consequence of the mostly linear dependence of the icosahedral energies as a function of the cluster composition, as is evident in Fig. 5, which plots the potential energies of the lowest energy icosahedral-like isomers for the Ar-core and Kr-core isomers. The overall trend is dominated by the large difference between the Ar and Kr intermolecular forces — as the fraction of Kr atoms increases, so too does the fraction of stronger Ar-Kr and Kr-Kr interactions. This effect overshadows the smaller, more subtle factors that influence the cluster structures. These can be made more evident by scaling out the gross linear dependence on cluster composition. The potential energies for the Ar-core and Kr-core icosahedral isomers as functions of cluster composition are shown again in Fig. 6, but in energy units scaled by the composition weighted average  $\epsilon_{\text{Avg}} = X_{\text{Ar}}\epsilon_{\text{Ar-Ar}} + X_{\text{Kr}}\epsilon_{\text{Kr-Kr}}$ , where  $X_{\text{Ar}} = n_{\text{Ar}}/(n_{\text{Ar}} + n_{\text{Kr}})$  and  $X_{\text{Kr}} = 1 - X_{\text{Ar}}$ . The lower plot shows the ground state Ar-core icosahedral-like configurations, while the upper plot shows their corresponding Kr-core isomers. To provide further insight into the interplay between the atomic size and the intermolecular potential, I have also included for comparison the energies of the minimized isomers resulting from having a common atomic size ( $\sigma_{\text{Ar-Ar}} = \sigma_{\text{Kr-Kr}}$ ,  $\Gamma = 1$ ), and those resulting from having a common well depth ( $\epsilon_{\text{Ar-Ar}} = \epsilon_{\text{Kr-Kr}}$ ,  $\alpha = 1$ ). For the Kr-core isomers, the curve is very similar to the  $\epsilon_{\text{Ar-Ar}} = \epsilon_{\text{Kr-Kr}}$  curve, indicating that it is the different atomic sizes that are the dominant influence in this case, while for the Ar-core isomers, the curve lies almost equidistant between the  $\epsilon_{\text{Ar-Ar}} = \epsilon_{\text{Kr-Kr}}$  and  $\sigma_{\text{Ar-Ar}} = \sigma_{\text{Kr-Kr}}$  curves, implying that neither factor predominates (it is slightly closer to the  $\sigma_{\text{Ar-Ar}} = \sigma_{\text{Kr-Kr}}$  curve).

The two sets of curves are complementary in the sense that the largest deviations from the homogeneous cluster values occur in each case for the isomers having a core atom of

one component surrounded by twelve atoms of the other component, while the smallest deviations occur for the isomers having a single atom of one component occupying an exterior site on the twelve-atom sub-cluster of the other component. Also, the directions of the deviations are reversed. For the ground state Ar-core isomers, setting  $\sigma_{\text{Ar-Ar}} = \sigma_{\text{Kr-Kr}}$  raises the scaled energy, while setting  $\epsilon_{\text{Ar-Ar}} = \epsilon_{\text{Kr-Kr}}$  lowers the scaled energy; the opposite is true for the Kr-core isomers.

Setting the Ar and Kr sizes equal and minimizing the resulting configurations isolates the effects of the intermolecular potential on the minimum energies of the two sets of isomers. For the Kr-core isomers, setting  $\sigma_{\text{Ar-Ar}} = \sigma_{\text{Kr-Kr}}$  effectively replaces the larger core atom with a smaller one, allowing the distended outer atoms to pack more tightly and thus lower the overall energy. The effect is most pronounced for  $\text{Ar}_{12}\text{Kr}$  since all twelve Ar atoms can move in a substantial amount; for  $\text{ArKr}_{12}$ , setting  $\sigma_{\text{Ar-Ar}} = \sigma_{\text{Kr-Kr}}$  is equivalent to replacing the smaller exterior Ar atom with a larger one, which has only a minor effect. The scaled energies are all less than that of homogeneous  $\text{Ar}_{13}$  because of the contributions from the stronger Ar-Kr and even stronger Kr-Kr interactions (much of the contribution from the Kr-Kr interactions has been incorporated into the energy scaling, but since the scaling is based only on the mole fraction and not on the actual distribution of the different interactions, small variations remain). For the Ar-core isomers, the opposite occurs; setting  $\sigma_{\text{Ar-Ar}} = \sigma_{\text{Kr-Kr}}$  effectively replaces the smaller core atom with a larger one, which moves the outer atoms out more and raises the overall energy. Analogously, the effect is most pronounced for  $\text{ArKr}_{12}$  since all twelve Kr atoms are distended a substantial amount, while for  $\text{Ar}_{12}\text{Kr}$ , only the larger exterior atom is replaced by a smaller one. The scaled energies for the Ar-core isomers are all greater than that of  $\text{Ar}_{13}$  because the central Ar atom decreases the number of Kr-Kr interactions relative to the weaker Ar-Kr and Ar-Ar interactions. These trends imply that the Kr-core icosahedral-like isomers would be the ground-state isomers if the two component atoms were actually the same size, and so there exists a critical size ratio for a given pair of binary cluster components where the isomers having the smaller atom (with the shallower well depth) at the core attain lower energies than those having the

larger atom (with the deeper well depth) at the core.

Setting the Ar and Kr well depths equal and minimizing the configurations isolates the effects of atomic size on the minimum energies of the two sets of isomers. For the Ar-core isomers, the scaled energy is lowered in each case, with the largest decrease occurring for  $\text{ArKr}_{12}$  and the smallest for  $\text{Ar}_{12}\text{Kr}$ . The effects can be more easily understood from the perspective of modifying the corresponding homogeneous clusters rather than from the modifications to the binary clusters themselves. In each of these two cases, setting  $\epsilon_{\text{Ar-Ar}} = \epsilon_{\text{Kr-Kr}}$  is equivalent to making one of the atoms of a homogeneous  $\text{Ar}_{13}$  or  $\text{Kr}_{13}$  cluster a different size. For  $\text{ArKr}_{12}$ , this atom would be the core atom, which effectively shrinks, again allowing all twelve of the exterior atoms to pack in more tightly and lower the energy, while for  $\text{Ar}_{12}\text{Kr}$ , this atom would be one of the exterior atoms, which effectively expands. This has a much smaller effect, though, since the atom is on the exterior. In a similar fashion for the Kr-core isomers, setting  $\epsilon_{\text{Ar-Ar}} = \epsilon_{\text{Kr-Kr}}$  is again equivalent to changing the sizes of some of the atoms of a homogeneous thirteen-atom cluster. For  $\text{Ar}_{12}\text{Kr}$ , the atom now effected would be the core atom, which becomes bigger, thus pushing all twelve of the outer Ar atoms outward and raising the overall energy a large amount, while for  $\text{ArKr}_{12}$ , the atom would be only one of the exterior atoms, which again would increase the energy only slightly. The energy increases relative to the homogeneous clusters are much larger for the Kr-core isomers than are the corresponding energy decreases for the Ar-core isomers; because of the repulsive steric constraints, the exterior Kr atoms in the Ar-core isomers are more restricted in their ability to collapse around the smaller Ar atom than are the exterior Ar atoms in the Kr-core isomers in their ability to distend outward from the larger Kr atom.

## B. Thermodynamic properties

The qualitative differences between the structural properties of the predominately Ar clusters and those of the predominately Kr clusters are found in their thermodynamic properties as well. Fig. 7 shows the heat capacity for each binary cluster as a function of

temperature. The J-walking curves in each case are the averages obtained from combining the results of the five individual J-walking runs, as described in Section II. Representative standard deviations have not been included to avoid cluttering the figures, but they were consistent with the noise levels in the curves. While the  $\text{Ar}_{12}\text{Kr}$  heat capacity curve is very similar to the  $\text{Ar}_{13}$  curve obtained previously<sup>26,41</sup> with a dominating peak in the solid-liquid transition region at 34 K, the  $\text{ArKr}_{12}$  curve is very much different, having a well separated second peak at 18 K. The heat capacity curve for each cluster in the series is characterized by a very large peak in the solid-liquid transition region at about 35 to 45 K, implying that each cluster still retains its magic number status, but significant changes are evident across the series from  $\text{Ar}_{12}\text{Kr}$  to  $\text{ArKr}_{12}$ . Analogous to the  $\text{Ar}_{13}$  case, the large size of the solid-liquid transition peak in each binary cluster is due to the correspondingly large energy difference between the ground-state icosahedral-like isomers and the higher energy non-icosahedral isomers, as well as to the large barriers to interconversion between the isomers. The variations in the peaks as the number of Kr atoms increases, and the ultimate appearance of the second peak in  $\text{ArKr}_{12}$ , are consequences mostly of energy differences occurring between the Ar-core and Kr-core isomers. The solid-liquid transition heat capacity peaks for those clusters having a substantial Ar fraction ( $\text{Ar}_{12}\text{Kr}$  to  $\text{Ar}_5\text{Kr}_8$ ) are mostly alike, showing only some minor differences in the peak heights, as well as a slight shifting of the peak position to higher temperatures as the number of Kr atoms increases. For the Kr-dominant clusters ( $\text{Ar}_4\text{Kr}_9$  to  $\text{ArKr}_{12}$ ), though, a smaller peak can be seen developing on the low temperature side of the solid-liquid transition peak, shifting downward in temperature with increasing Kr numbers, until becoming well separated at  $\text{ArKr}_{12}$ . As was seen in Fig. 4, the energy difference between the Ar-core and Kr-core icosahedral-like isomers decreases steadily and rapidly across the series. The Kr-core icosahedral-like isomers first separate from the large non-icosahedral band at  $\text{Ar}_7\text{Kr}_6$ , become approximately equidistant between the ground-state Ar-core icosahedral-like group and the non-icosahedral band by  $\text{Ar}_4\text{Kr}_9$ , and finally attain their nearest approach to the ground state at  $\text{ArKr}_{12}$ . Thus for the predominately Ar clusters, the Kr-core icosahedral-like isomers are too high in energy to be accessible at

temperatures below the solid-liquid transition region, but for the clusters  $\text{Ar}_3\text{Kr}_{10}$  to  $\text{ArKr}_{12}$ , the Kr-core icosahedral-like isomers are sufficiently low lying in energy that they contribute to the heat capacity at temperatures well below the solid-liquid transition region.

The standard Metropolis heat capacity curves for each cluster are also included in Fig. 7. These are in good agreement with the J-walking curves only for the predominantly Ar clusters. For  $\text{Ar}_{12}\text{Kr}$  to  $\text{Ar}_9\text{Kr}_4$ , the Metropolis solid-liquid transition peaks are about 5 to 10% too low, but otherwise compare well with their J-walking counterparts. This is comparable to the size of the discrepancies found previously for  $\text{Ar}_{13}$ .<sup>26,41</sup> For  $\text{Ar}_8\text{Kr}_5$  to  $\text{Ar}_3\text{Kr}_{10}$ , though, there are substantial discrepancies between the Metropolis and J-walking curves evident on the low temperature side of the solid-liquid transition peak, and for  $\text{Ar}_2\text{Kr}_{11}$  and  $\text{ArKr}_{12}$ , the low temperature shoulder and peak, respectively, are completely absent in the Metropolis curves. The deficiency of the standard Metropolis algorithm in application to binary clusters in this temperature regime can also be seen by comparing the results to those obtained using the atom-exchange method, which have been included for the clusters  $\text{Ar}_6\text{Kr}_7$  to  $\text{ArKr}_{12}$ . In each case, the atom-exchange results are in good agreement with the J-walker results, with the exception of the transition peak heights again being slightly too low. Even the smaller low temperature peak in  $\text{ArKr}_{12}$  was well reproduced with the atom-exchange method. Because the atom-exchange method is just the standard Metropolis algorithm augmented with an occasional swapping of atoms from the different components, it is clear that the Kr-core icosahedral isomers are not being accessed dynamically during the course of the Metropolis walks at these temperatures, but only via the exchange mechanism (or from the stored distributions in the case of the J-walking runs).

The slight energy differences between the various Ar-core icosahedral-like permutational isomers result in the very small mixing-anomaly peaks that occur at very low temperatures (about 1 to 5 K) in Fig. 7. In general, the size of each peak is a function of the number of Ar-core icosahedral-like isomers present —  $\text{Ar}_{12}\text{Kr}$ ,  $\text{Ar}_2\text{Kr}_{11}$  and  $\text{ArKr}_{12}$  each have only one Ar-core icosahedral-like isomer and thus do not exhibit this low temperature mixing-anomaly peak (although  $\text{Ar}_2\text{Kr}_{11}$  and  $\text{ArKr}_{12}$  show mixing between the ground state Ar-core isomer

and the Kr-core isomers),  $\text{Ar}_{11}\text{Kr}_2$  and  $\text{Ar}_3\text{Kr}_{10}$  each have just three closely spaced Ar-core icosahedral-like permutational isomers that can contribute to the heat capacity and so have barely discernible mixing-anomaly peaks, while all the remaining clusters from  $\text{Ar}_{10}\text{Kr}_3$  to  $\text{Ar}_4\text{Kr}_9$  have enough low lying Ar-core icosahedral-like permutational isomers that the mixing-anomaly peak in each case is clearly noticeable. The peak heights are all very small, less than five reduced units from the baseline. Considering that the standard Metropolis method was unable to handle the transitions to the low lying Kr-core icosahedral-like isomers in  $\text{Ar}_2\text{Kr}_{11}$  and  $\text{ArKr}_{12}$ , it is not surprising then that the method was also unable to reproduce the mixing-anomaly peaks. The atom-exchange results show some smaller peaks, but they are not in good agreement with the J-walking results. This can be seen better in Fig. 8, which shows the low-temperature parts of the heat capacity curves obtained from each of the three methods in greater detail for all the clusters having more than one Ar-core icosahedral-like isomer. The atom-exchange curves are all in good agreement with the J-walking curves on the high temperature tails of the peaks, but each drops off rapidly, joining the Metropolis curves well before the peak temperature. This is a consequence of the atom-exchange method failing as the temperature becomes too low. At such low temperatures, most of the Metropolis configurations have energies only slightly above their nearest local minimum so that the trial configurations most likely obtained by exchanging an exterior Ar atom with an exterior Kr atom will be a strained configuration having too high an energy to be accepted. The dependence of the peak size on the number of Ar-core isomers can also be seen more clearly:  $\text{Ar}_7\text{Kr}_6$  has the most isomers with eighteen, and has the largest peak;  $\text{Ar}_8\text{Kr}_5$  and  $\text{Ar}_6\text{Kr}_7$  with twelve isomers each, and  $\text{Ar}_9\text{Kr}_4$  and  $\text{Ar}_5\text{Kr}_8$  with ten each, have similarly sized peaks;  $\text{Ar}_{10}\text{Kr}_3$  and  $\text{Ar}_4\text{Kr}_9$  with five isomers each have much smaller peaks, and  $\text{Ar}_{11}\text{Kr}_2$  and  $\text{Ar}_3\text{Kr}_{10}$  with only three isomers each have the smallest peaks (which are actually only shoulders). The peak widths also depend on the energy spread between the different isomers. For example  $\text{Ar}_{10}\text{Kr}_3$  has a smaller energy spread than does  $\text{Ar}_4\text{Kr}_9$  ( $\Delta E = E_4 - E_0 = 0.12115$  compared to  $0.16146$ ), and thus it has a narrower peak.

Lopez and Freeman<sup>15</sup> estimated the entropy change associated with the low tempera-

ture isomerization transition for  $\text{Pd}_6\text{Ni}_7$  by numerically integrating their heat capacity data according to the expression

$$\Delta S_t = \int_0^{T_1} \frac{\Delta C_V dT}{T}, \quad (4)$$

where  $T_1$  was the temperature just above the mixing anomaly, and  $\Delta C_V$  was the difference between the J-walking and Metropolis heat capacities (the assumption being that the J-walking results reflected complete access to all the permutational isomers over the temperature range, while the system was stuck in its lowest-energy configuration during the Metropolis runs so that none of the permutational isomers were accessed). They obtained a value of  $\Delta S_t/k_B = 4.8$ . I have followed Lopez and Freeman and have calculated the entropy changes from the heat capacity data shown in Fig. 8 by numerically integrating Eq. 4. The results are plotted in Fig. 9. The entropy changes mostly support the qualitative observations given earlier, that the peak sizes are related to the number of closely spaced Ar-core icosahedral-like permutational isomers, except for the curious inversion of the values for  $\text{Ar}_8\text{Kr}_5$  and  $\text{Ar}_6\text{Kr}_7$  (both with twelve isomers), which are slightly lower than those for  $\text{Ar}_9\text{Kr}_4$  and  $\text{Ar}_5\text{Kr}_8$  (both with ten isomers). The curve is nearly symmetrical about  $\text{Ar}_7\text{Kr}_6$ , consistent with the symmetry in the numbers of Ar-core isomers. The maximum value (4.4) occurring for  $\text{Ar}_7\text{Kr}_6$  is similar to Lopez and Freeman's value for the analogous metal cluster  $\text{Pd}_6\text{Ni}_7$ .

The shifting of the solid-liquid transition peaks to higher temperatures as the Kr fraction increases, as well as the variation in the peak heights, is presented in more detail in Fig. 10; the peak heights and temperatures are also listed in Table III. These values were obtained in each case from the averaged J-walker curves shown in Fig. 7. The curves were smoothed and then interpolated in the peak vicinities to obtain finer mesh sizes. The peak parameters were then found simply by searching the interpolated data. Some minor variations in the peak parameter values thus obtained occurred when different smoothing parameters were used,<sup>61</sup> but these were much smaller than the uncertainties obtained from averaging the individual J-walker runs, and so a single common set of smoothing parameters was used

for each case, with the uncertainties in the peak heights then estimated from the average standard deviations of the points in the vicinity of each peak. The uncertainties in the peak height were all less than 1%, and the uncertainties in the peak temperature less than 0.5%. The values for  $\text{Ar}_{13}$  ( $118.5 \pm 0.6$  at  $34.05 \pm 0.06$  K) and scaled  $\text{Kr}_{13}$  ( $118.0 \pm 0.6$  at  $34.05 \pm 0.07$  K) are in good agreement with the values I obtained previously ( $117.7 \pm 0.2$  at  $34.33 \pm 0.08$  K),<sup>41</sup> and with the values obtained by Tsai and Jordan ( $117.1$  at  $34.15$  K).<sup>27,62</sup> Table III also lists the mixing-anomaly peak parameters for those clusters having distinct peaks.

As is evident in Fig. 10, there is a nearly linear increase in the peak temperature as a function of cluster composition from  $\text{Ar}_{13}$  (34.05 K) to  $\text{Ar}_7\text{Kr}_6$  (37.05 K), followed by another nearly linear, but more rapid increase in the peak temperature for the clusters  $\text{Ar}_6\text{Kr}_7$  (37.63 K) to  $\text{Kr}_{13}$  (46.77 K). The peak heights show a more interesting variation. They increase initially as the fraction of Kr atoms increases from  $\text{Ar}_{13}$ , reaching a maximum at  $\text{Ar}_9\text{Kr}_4$ . They then continue decreasing until reaching a minimum at  $\text{Ar}_3\text{Kr}_{10}$ , before rising again until they reach their original height again at  $\text{Kr}_{13}$ . This complementary behavior is consistent with the differences in the cluster minimum energies between the Ar-dominant and Kr-dominant clusters. It should be kept in mind, though, that these variations are relatively small (the difference between the maximum and minimum peak heights is only about 12% of the  $\text{Ar}_{13}$  peak height) and that the heat capacity peak heights are in fact remarkably similar considering the degree of change seen in the cluster structural properties as functions of composition.

The potential energy curve for each cluster as a function of temperature is shown in Fig. 11. Except for the  $\text{ArKr}_{12}$  curve, the curves all appear very similar in shape and show roughly uniform spacing. This again is a consequence of the mostly linear dependence of the isomer energies on the cluster composition. The low temperature part of the curves is dominated by the energetics of the Ar-core icosahedral-like isomers and thus exhibit much the same linear dependence with cluster composition as was seen in Fig. 5, while the high temperature part of the curves is dominated by various dissimilar liquid-like structures that

are well mixed. In this regime, the clusters are sufficiently distended that the intermolecular interactions predominate over the size constraints, resulting in curves having almost uniform displacements.

### C. Quench results

The temperature dependence of the binary cluster isomerizations can also be inferred from the quench studies. Figs. 12 and 13 show the results obtained using J-walking for the Ar-predominate and Kr-predominate clusters, respectively; quench results for  $\text{Ar}_{13}$  have also been included in Fig. 12 for comparison. The large energy gap between the  $\text{Ar}_{13}$  ground state icosahedral isomer and the next lowest energy isomers is reflected in the quench curves — all the configurations quenched to the icosahedral isomer, up to a temperature of 25 K, and half the configurations quenched to the icosahedral isomer at the heat capacity peak temperature of 34 K. Even at a temperature of 45 K, which is well into the liquid region, about 10% of the quenches were to the lowest energy isomer. The next three lowest energy isomers (the truncated icosahedral isomers having a lone displaced atom located on one of the icosahedral faces) are closely spaced in energy and well separated from the next highest energy isomer. Their quench curves are likewise very similar, forming a distinct group of curves slowly rising from zero at about 28 K. These three isomers and the lowest energy isomer dominate the cluster dynamics in the transition region; at the heat capacity peak temperature, they comprise 80% of the quenched configurations. Given the similarity between the  $\text{Ar}_{13}$  and  $\text{Ar}_{12}\text{Kr}$  isomer energy spectra shown in Fig. 4, it is not surprising that their quench curves are also similar. The group of three closely spaced  $\text{Ar}_{13}$  truncated icosahedral isomers becomes a slightly broader group of twenty similar  $\text{Ar}_{12}\text{Kr}$  permutational isomers, but the quench profile for this group of isomers is similar to the profile for the three  $\text{Ar}_{13}$  isomers.

$\text{Ar}_{11}\text{Kr}_2$  has three Ar-core icosahedral-like permutational isomers closely spaced in energy that can be accessed at very low temperatures, and this is evident in the quench curves.

The curves are roughly constant over the domain 15 K to 30 K, with the two lowest energy isomers being predominate, comprising about 90% of the quenched configurations. The apparent deficiency of quenches for the third isomer can be explained simply in terms of the number of equivalent configurations. As shown in Fig. 3, this isomer has the two Kr atoms occupying the axial positions of the icosahedron. The number of ways the two Kr and eleven Ar atoms can be combined to form this icosahedral isomer is much smaller than the number of ways the other two isomers can be formed. The behavior at the heat capacity peak temperature is similar to that of  $\text{Ar}_{13}$  and  $\text{Ar}_{12}\text{Kr}$ , with the number of Ar-core icosahedral quenches decreasing quickly and the number of non-icosahedral quenches rising rapidly. The  $\text{Ar}_{10}\text{Kr}_3$  curves are similar to the  $\text{Ar}_{11}\text{Kr}_2$  curves, except that  $\text{Ar}_{10}\text{Kr}_3$  has five closely spaced Ar-core icosahedral-like permutational isomers. As the temperature increases from zero, each isomer is accessed in order according to its energy, but over the range 10 K to 30 K where the curves show plateaus, the levels are determined by the combinatorics. Thus the ground state isomer having its three Kr atoms occupying adjacent icosahedral sites has the second lowest number of quenches over this region.

The plots for the clusters  $\text{Ar}_9\text{Kr}_4$  to  $\text{Ar}_5\text{Kr}_8$  were mostly similar to the  $\text{Ar}_{10}\text{Kr}_3$  plot, except that they had many more low lying Ar-core icosahedral-like permutational isomers, and so these plots have not been included. For the Kr-predominate clusters, though, the relatively low lying Kr-core icosahedral-like permutational isomers can also be seen to effect the quench curves. Like  $\text{Ar}_{10}\text{Kr}_3$ ,  $\text{Ar}_4\text{Kr}_9$  has five closely spaced Ar-core icosahedral-like permutational isomers. It also has ten closely spaced Kr-core icosahedral-like permutational isomers having energies roughly equidistant between the ground state isomer and the non-icosahedral isomers. As can be seen in Fig. 3, the arrangements of the three non-core Ar atoms in each of the five  $\text{Ar}_4\text{Kr}_9$  Ar-core icosahedral-like isomers is the same as the arrangements of the three Kr atoms in each of the corresponding  $\text{Ar}_{10}\text{Kr}_3$  isomers, and so the low-temperature parts of their quench curves are similar, with the isomers showing the same ranking in the number of quenched configurations in the plateau region (and nearly the same levels). The quenched  $\text{Ar}_4\text{Kr}_9$  Kr-core icosahedral-like permutational isomers begin to

appear at about 20 K, which is consistent with the broadening of the solid-liquid transition region heat capacity peak seen in Fig. 7. The non-icosahedral isomers first appear at about 25 K, similar to the other clusters.

Analogously, both  $\text{Ar}_3\text{Kr}_{10}$  and  $\text{Ar}_{11}\text{Kr}_2$  have three low lying Ar-core icosahedral-like permutational isomers, with the two exterior Ar atoms in  $\text{Ar}_3\text{Kr}_{10}$  having the same three arrangements as the two Kr atoms in  $\text{Ar}_{11}\text{Kr}_2$ . Again the quench curves for the three  $\text{Ar}_3\text{Kr}_{10}$  isomers are very similar to the corresponding three  $\text{Ar}_{11}\text{Kr}_2$  isomers at temperatures below 20 K, but the  $\text{Ar}_3\text{Kr}_{10}$  curves begin to drop off at this point as the five Kr-core icosahedral-like permutational isomers begin to be accessed. The Kr-core isomers are close enough in energy to the Ar-core icosahedral-like isomers that their quench curves can be seen to be well separated from the non-icosahedral isomers, unlike the case for the other binary clusters having a greater Ar fraction. This trend continues with increasing Kr fraction.  $\text{Ar}_2\text{Kr}_{11}$  has only one Ar-core icosahedral-like isomer, and so the three Kr-core icosahedral-like isomers are the next isomers accessed, beginning at about 15 K. Finally, with  $\text{ArKr}_{12}$ , the Kr-core icosahedral-like isomer is so much closer in energy to the Ar-core icosahedral-like ground state than it is to the non-icosahedral isomers that 90% of the quenches at 35 K, where the non-icosahedral isomers begin to be accessed, are to the Kr-core isomer. Note that while both isomers each have half of the quenched configurations at 20 K, a temperature near the heat capacity peak temperature, this does not imply that there is a dynamic equilibrium between the two. The barrier height for moving an Ar atom from the core to an exterior site while a Kr atom moves into the core is too high to overcome at these temperatures, as is implied by the fact that the peak is not reproduced at all using the standard Metropolis method.

#### IV. CONCLUSION

Binary clusters whose component atoms are not too dissimilar retain many of the features of their simpler homogeneous counterparts, but have additional parameters such as the

cluster composition and mixing rules that can be “tuned” to modify their properties and provide more insight into their physical behavior. Much of the physical behavior of thirteen-atom Ar-Kr clusters was very similar to that of  $\text{Ar}_{13}$ , especially for those clusters having a low Kr fraction, but several changes that occurred as the Kr fraction increased resulted in the predominantly Kr clusters being quite different. These changes were not so drastic, though, that they radically altered the physical properties — even  $\text{ArKr}_{12}$ , which was the most dissimilar of the set, still retained the icosahedral-like ground-state and the magic-number behavior characteristic of homogeneous thirteen-atom clusters. Replacing Ar atoms in  $\text{Ar}_{13}$  by Kr atoms may have modified the potential energy hypersurface considerably, and in the case of the predominately Kr clusters led to several isomers having energies within the large gap between the icosahedral global minimum and the non-icosahedral local minima, but the hypersurface still retained the characteristic deep wells and large barriers associated with the icosahedral-like isomers that dominate the solid-liquid transition behavior.

The changes in the Ar-Kr clusters’ heat capacity behavior as the Kr fraction increased were primarily due to the Ar-core and Kr-core icosahedral-like permutational isomers. Although the Ar and Kr sizes are similar enough that all the binary clusters in the series had icosahedral-like isomers as their lowest energy configurations, the size difference is large enough that the central atom in each case was an Ar atom, instead of a Kr atom, which would have been the case had their sizes been equal. For the predominately Ar clusters, the Kr-core icosahedral-like isomers were too high in energy to have had much effect on the clusters’ low-temperature behavior, but as the Kr fraction increased across the series, the Kr-core icosahedral-like isomers rapidly dropped in energy, so that for the predominately Kr clusters, they began to dominate the clusters’ low-temperature behavior, eventually forming a distinct second, lower temperature, heat capacity peak. The Ar-core icosahedral-like permutational isomers manifested themselves as the very small mixing-anomaly peaks that occurred at very low temperatures. These peaks had sizes that depended primarily on the number of Ar-core permutational isomers, since the energy differences between these isomers were quite small. The mixing-anomaly peak was largest for  $\text{Ar}_7\text{Kr}_6$ , which has the

most Ar-core permutational isomers.

Since the mixing-anomaly heat capacity peaks are due to the presence of several closely spaced isomers having energies only slightly above that of the lowest-energy isomer, one may wonder why similar, very small, low-temperature peaks have not been previously observed in homogeneous clusters likewise having low lying isomers whose energies lie slightly above their ground-state isomer. For example,  $\text{Ar}_{17}$  has a low lying isomer with an energy of  $-61.307$  that lies only slightly above the ground-state isomer energy of  $-61.318$ .<sup>63</sup> In my previous study of Lennard-Jones cluster heat capacities,<sup>41</sup> neither the  $N = 17$  curve nor any of the other heat capacity curves I calculated for cluster sizes ranging from four to twenty-four atoms had such peaks, although curves for  $N = 18$  and  $21$  showed very small, low temperature, “bumps” that might be suitable candidates. Since the major emphasis in those calculations was the characterization of magic-number behavior in the solid-liquid transition region, I did not extend the J-walking distributions down to the very low temperatures that I did in this study,<sup>64</sup> nor did I perform quench calculations to determine the energetics of the low-lying isomers. Thus it is possible some of those clusters actually have very small, low temperature, peaks that were simply missed, although it is not likely for most since their small sizes imply they do not have many isomers near the ground-state. As the cluster size increases, though, the number of isomers increases rapidly, and so some larger clusters could be expected to also possess small low-temperature peaks in their heat capacity curves. Preliminary heat capacity calculations I have done on medium sized Lennard-Jones clusters have found such peaks for  $N = 31, 32$  and  $33$ , but not for  $N = 25$  to  $30$  (I have not yet done calculations for  $N > 33$ ).  $N = 31$  corresponds to a critical size in Lennard-Jones cluster structures, in the sense that it marks the crossover point for their preferred sublattice topologies. In his study of the structure and binding of Lennard-Jones clusters for  $13 \leq N \leq 147$ , Northby<sup>38</sup> distinguished between two types of sublattice structures: the “IC” sublattice, which consists of all the sites that will comprise the outer shell of the next complete Mackay icosahedron, and the “FC” sublattice, which consists of those tetrahedrally bonded face sites that lie at stacking fault locations relative to the first lattice, together with

the vertex sites. For  $N < 31$ , each of the cluster’s lowest energy isomers had an FC topology, while for  $31 \leq N \leq 55$ , each had an IC topology. The small heat capacity peaks for  $N = 31$ , 32, and 33 appear therefore to reflect a “phase” transition between the two different types of structures.

The calculations presented here have demonstrated again that the standard Metropolis algorithm is inadequate for dealing with the low-temperature behavior of heterogeneous clusters. Augmenting the Metropolis method with the atom-exchange method improved its accuracy greatly, and so should be done routinely on multicomponent simulations where J-walking is not done, to provide reasonable reliability in this regime. But even the atom-exchange method does not reduce the problems due to quasiergodicity to the extent that the J-walking method does. The J-walking calculations for binary clusters were more complicated than those done on similar homogeneous clusters because of the greater possibility for systematic errors corrupting the J-walker distributions, which necessitated the use of multiple trials from independently generated distributions to ensure that such errors were not present. However, this computational overhead was mitigated by the shorter walk lengths required for J-walking to achieve the desired level of accuracy compared to the Metropolis method; for example, for  $\text{Ar}_8\text{Kr}_5$ , five J-walker runs of  $10^6$  passes each provided a level of accuracy in the solid-liquid transition region that required runs totalling  $10^8$  passes for the Metropolis method to match.

Calculations on Ne-Ar clusters similar to the ones reported here for Ar-Kr clusters are nearing completion and will be submitted for publication shortly. The interaction parameters for Ne and Ar are much more dissimilar than are the Ar and Kr interaction parameters ( $\epsilon_{\text{Ne-Ne}}/\epsilon_{\text{Ar-Ar}} = 0.2982$  compared to  $\epsilon_{\text{Ar-Ar}}/\epsilon_{\text{Kr-Kr}} = 0.7280$ ). More importantly though, the Ne and Ar atomic sizes are considerably more dissimilar than are the Ar and Kr sizes ( $\sigma_{\text{Ne-Ne}}/\sigma_{\text{Ar-Ar}} = 0.8073$  compared to  $\sigma_{\text{Ar-Ar}}/\sigma_{\text{Kr-Kr}} = 0.8897$ ). This size differential is sufficiently large that not all the Ne-Ar clusters retain the icosahedral-like symmetry for their ground-state configurations, and a much greater diversity of structures is obtained. Not surprisingly, this leads to very much different behavior in the Ne-Ar clusters’ heat capacities.

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<sup>62</sup> Since the constraining radius was constant at  $3\sigma_{\text{Kr-Kr}}$  for all runs, the law of corresponding states implies that the  $\text{Kr}_{13}$  simulations are equivalent to  $\text{Ar}_{13}$  simulations using a smaller constraining sphere. Similarly, the other values listed were obtained from simulations using different constraining radii, and so minor discrepancies in the peak parameters are not unexpected.

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<sup>64</sup> At such low temperatures, the J-walking runs effectively became Metropolis walks since none of the attempted jumps were accepted. More intermediate temperature J-walker distributions would have been needed to fully characterize this region.

## FIGURES

FIG. 1. Heat capacity curves for  $\text{Ar}_8\text{Kr}_5$  clusters. The large peak corresponds to the solid-liquid transition region, while the small low-temperature peak is due to the icosahedral-like permutational isomers. The five solid curves were obtained from separate J-walking runs, each using a different set of J-walker distributions, initially generated at 52 K. The data for each temperature were obtained from  $10^6$  total passes. The differences between the curves are comparable to the noise levels inherent in each, indicating that the systematic errors associated with each J-walker distribution were sufficiently small. For comparison, the dotted curves show the results obtained from similar J-walker runs using sets of J-walker distributions initially generated at 70 K, a temperature high enough for the cluster to be completely dissociated. Systematic errors in the high temperature J-walker distributions can be seen to have not only slightly effected the solid-liquid transition peak, but to have also propagated through the subsequent distributions to substantially effect the low temperature peak. Also included is the dashed curve obtained from standard Metropolis runs having  $10^7$  total passes of data accumulation at each temperature. The curve was begun at the lowest temperature using the lowest energy isomer as the initial configuration, with the final configuration at each temperature then used as the initial configuration for the next temperature. Substantial discrepancies due to quasiergodicity are evident in the solid-liquid transition region, and the low-temperature mixing-anomaly peak is completely absent. The open circles, representing Metropolis results obtained using  $10^8$  total passes, are in agreement with the J-walker results. Augmenting standard Metropolis with the atom-exchange algorithm does improve its low temperature performance, as can be seen by the long-dashed curve, which shows a small mixing-anomaly peak. However, substantial discrepancies still remain.

FIG. 2. Lowest energy configurations for  $\text{Ar}_{13}$  clusters obtained from quenches of clusters stored in the J-walker distribution files. The energies are in reduced units,  $E^* = E/\epsilon_{\text{Ar-Ar}}$ . Except for the two metastable structures (indicated by the parentheses) these configurations are identical to the lowest-lying isomers given in Refs. 59 and 60. The four lowest energy stable isomers are the topological forms for all the lowest energy Ar-Kr isomers shown in Fig. 3.

FIG. 3. The thirteen lowest energy isomers found for  $\text{Ar}_{13-n}\text{Kr}_n$  clusters ( $1 \leq n \leq 12$ ), in order of increasing energy; their energies are listed in Table II. The isomers were obtained from quenches of configurations stored in J-walker distribution files. In each case, the ground state isomer is an icosahedral-like configuration having an Ar atom as the central atom. For those clusters having several permutational isomers, the segregated isomers have lower energies than the mixed isomers.

FIG. 4. Local potential energy minima (in reduced units) for  $\text{Ar}_{13-n}\text{Kr}_n$  clusters ( $0 \leq n \leq 13$ ). In each case, the zero energy level corresponds to the global minimum energy. The triangles mark the lowest-energy icosahedral-like permutational isomers having a Kr atom as the central atom.

FIG. 5. Binary cluster potential energies for the lowest energy icosahedral-like isomers, as functions of composition. The filled circles represent the lowest energy isomers having a central Ar atom, while the open circles represent the lowest energy isomers having a central Kr atom (indicated by the triangles in Fig. 4).

FIG. 6. Binary cluster minimum energies as a function of composition. Energies are scaled by the composition weighted average  $\epsilon_{\text{Avg}} = X_{\text{Ar}}\epsilon_{\text{Ar-Ar}} + X_{\text{Kr}}\epsilon_{\text{Kr-Kr}}$ , where  $X_{\text{Ar}} = n_{\text{Ar}}/(n_{\text{Ar}} + n_{\text{Kr}})$  and  $X_{\text{Kr}} = 1 - X_{\text{Ar}}$ . Ground state isomers are indicated in the lower plot by the filled circles, while the corresponding lowest-energy Kr-core isomers are indicated in the upper plot by the open circles. Also shown for comparison are the results for the artificial cases where the two components have same atomic sizes or the same well depths; the triangles indicate the minimum energies obtained when  $\sigma_{\text{Ar-Ar}}$  was set equal to  $\sigma_{\text{Kr-Kr}}$  ( $\Gamma = 1$ ) and each configuration reminimized, while the squares indicate the minimum energies that resulted when  $\epsilon_{\text{Ar-Ar}}$  was set equal to  $\epsilon_{\text{Kr-Kr}}$  ( $\alpha = 1$ ) and the isomers reminimized.

FIG. 7. Heat capacities for the binary clusters  $\text{Ar}_{13-n}\text{Kr}_n$  ( $1 \leq n \leq 12$ ). In each case, the thick curve represents the J-walking results and the thin curve the standard Metropolis results; the open circles represent the results obtained using Metropolis Monte Carlo augmented with the atom-exchange algorithm. Increasingly larger discrepancies between the Metropolis and J-walking results over much of the temperature ranges are evident as the mole fraction of Kr increases. The agreement between the J-walking results and those obtained using the atom-exchange method is mostly very good except at very low temperatures. Expanded views of the low temperature region can be seen in Fig. 8.

FIG. 8. Low temperature heat capacity curves for those binary Ar-Kr clusters exhibiting low temperature mixing-anomaly peaks. In each case, the thick curve represents the J-walking results and the thin curve the standard Metropolis results; the dotted curves represent the results obtained using Metropolis Monte Carlo augmented with the atom-exchange algorithm. The peaks are due to the low lying Ar-core icosahedral-like permutational isomers, and tend to be largest for those clusters having the largest number of such isomers; the numbers in parentheses indicate the number of isomers found in each case (these are in agreement with the values obtained from the binary icosahedral cluster atom counting rules in Ref. 13). The atom-exchange results are in qualitative agreement with the J-walking results, but show increasingly large discrepancies as the temperature decreases. The standard Metropolis algorithm was unable to reproduce the peaks at all. The heat capacity peak areas as a function of cluster composition are shown in Fig. 9.

FIG. 9. Entropy changes associated with the low temperature permutational isomerization transitions shown in Fig. 8 (circles). These were obtained by numerically integrating the low temperature heat capacity differences according to Eq. 4 in the text. Also shown for a qualitative comparison are  $\Delta S/k_B = \ln N_{\text{Ar}}$  (squares), where  $N_{\text{Ar}}$  is the number of low-lying Ar-core icosahedral-like permutational isomers. The curves are symmetric about  $\text{Ar}_7\text{Kr}_6$ .

FIG. 10. Solid-liquid transition heat capacity peak trends for thirteen-atom Ar-Kr clusters. The top plot shows the transition peak temperatures as a function of cluster composition, while the middle plot shows the transition peak heights as a function of composition. The bottom plot depicts the peak heights as a function of the peak temperature. The peak height error bars are single standard deviations obtained from averaging the individual J-walker runs; the standard deviations in the peak temperatures are smaller than the symbol size. The peak temperature and height for each cluster also are listed in Table III. The curves have been added merely as a visual aid.

FIG. 11. Potential energy curves as functions of temperature for  $\text{Ar}_{13-n}\text{Kr}_n$  clusters ( $0 \leq n \leq 13$ ). The curves were obtained using J-walking.

FIG. 12. Quench results for the Ar-predominate clusters. These were obtained by periodically quenching cluster configurations by steepest descent every 1000 passes during one of the J-walker runs, giving 1000 quenched configurations for each temperature. The dotted vertical lines in each plot indicate the solid-liquid heat capacity peak temperature, the dashed line in the  $\text{Ar}_{10}\text{Kr}_3$  plot the mixing-anomaly heat capacity peak temperature. The dotted curve in the  $\text{Ar}_{13}$  plot is the sum of the  $-41.4720$ ,  $-41.4446$  and  $-41.3944$  curves for the truncated icosahedral-like isomers having one of the atoms displaced onto an icosahedral face. The curve is similar to the corresponding curve shown in the  $\text{Ar}_{12}\text{Kr}$  plot representing the sum of the topologically similar permutational isomers (energies ranging from  $-42.8345$  to  $-42.5546$ ).

FIG. 13. J-walker quench results for the Kr-predominate clusters. The  $\text{Ar}_3\text{Kr}_{10}$  curves are similar to the  $\text{Ar}_{11}\text{Kr}_2$  curves at low temperatures, reflecting their complementary permutations ( $\text{Ar}_{11}\text{Kr}_2$  has three unique ways to position its two exterior Kr atoms, while  $\text{Ar}_3\text{Kr}_{10}$  has three unique ways to position its two exterior Ar atoms). Likewise, the  $\text{Ar}_4\text{Kr}_9$  and  $\text{Ar}_{10}\text{Kr}_3$  curves are similar at low temperatures, reflecting their five complementary permutations.

# TABLES

TABLE I. Lennard-Jones parameters used in the calculations. The Ar-Ar and Kr-Kr parameters were obtained from Ref. 50. The Ar-Kr parameters were obtained from the usual Lorentz-Berthelot mixing rules, with  $\epsilon_{\text{Ar-Kr}} = (\epsilon_{\text{Ar-Ar}} \epsilon_{\text{Kr-Kr}})^{1/2}$  and  $\sigma_{\text{Ar-Kr}} = \frac{1}{2}(\sigma_{\text{Ar-Ar}} + \sigma_{\text{Kr-Kr}})$ .

Parameter	Ar-Ar	Ar-Kr	Kr-Kr
$\epsilon/\text{K}$	119.4	139.9	164.0
$\sigma/\text{\AA}$	3.405	3.616	3.827

TABLE II. Potential energies for the thirteen lowest-energy equilibrium configurations shown in Fig. 3. These values were obtained from quench studies of the configurations stored in the J-walker distribution files. The energies are expressed in units of  $-\epsilon_{\text{Ar-Ar}}$ .

Isomer	Ar <sub>13</sub>	Ar <sub>12</sub> Kr	Ar <sub>11</sub> Kr <sub>2</sub>	Ar <sub>10</sub> Kr <sub>3</sub>	Ar <sub>9</sub> Kr <sub>4</sub>	Ar <sub>8</sub> Kr <sub>5</sub>	Ar <sub>7</sub> Kr <sub>6</sub>
0	44.32680	45.63591	46.96682	48.33095	49.67668	51.00709	52.36758
1	41.47198	42.83445	46.93058	48.28062	49.62872	50.94539	52.32164
2	41.44460	42.82518	46.91792	48.24762	49.58362	50.91443	52.30801
3	41.39440	42.80750	44.22434	48.23388	49.58077	50.91220	52.26145
4	40.75851	42.74808	44.21728	48.20980	49.56613	50.90030	52.22974
5	40.72846	42.74772	44.19670	45.65087	49.54682	50.89607	52.20526
6	40.71041	42.73919	44.13587	45.56089	49.53680	50.86535	52.20152
7	40.67380	42.70903	44.12606	45.54767	49.53207	50.85777	52.19877
8	40.67017	42.70607	44.12033	45.52440	49.52140	50.85168	52.19756
9	40.61547	42.69850	44.10625	45.51355	49.51229	50.83533	52.18107
10	40.60458	42.68338	44.09642	45.50997	46.97535	50.83188	52.17493
11	40.54129	42.67932	44.09642	45.47972	46.90413	50.82146	52.16898
12	40.43333	42.66306	44.07858	45.46893	46.88614	48.29016	52.16469
Isomer	Kr <sub>13</sub>	ArKr <sub>12</sub>	Ar <sub>2</sub> Kr <sub>11</sub>	Ar <sub>3</sub> Kr <sub>10</sub>	Ar <sub>4</sub> Kr <sub>9</sub>	Ar <sub>5</sub> Kr <sub>8</sub>	Ar <sub>6</sub> Kr <sub>7</sub>
0	60.88438	60.20496	58.85534	57.54709	56.26291	54.96607	53.65239
1	56.96319	59.26313	57.68168	57.48759	56.22254	54.92236	53.59395
2	56.92558	56.18509	57.63023	57.47117	56.16076	54.87811	53.57622
3	56.85663	56.15784	57.62012	56.12257	56.14611	54.86568	53.56163
4	55.98322	56.13239	55.36065	56.08925	56.10145	54.84450	53.54690
5	55.94194	56.10745	55.34242	56.03676	54.55578	54.81735	53.53000
6	55.91714	56.10706	55.28127	56.02826	54.51999	54.80451	53.50389
7	55.86686	56.02651	55.01280	55.98787	54.48346	54.80224	53.49223
8	55.86188	55.57558	55.00157	54.24192	54.47720	54.78820	53.48683

9	55.78674	55.56758	54.98270	54.23330	54.45869	54.75605	53.46915
10	55.77179	55.54524	54.98117	54.21973	54.43440	52.97815	53.45425
11	55.68486	55.53571	54.96068	54.21746	54.42764	52.93491	53.44179
12	55.53657	55.50822	54.90435	54.20269	54.42467	52.91667	51.42744

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TABLE III. Heat capacity peak parameters for thirteen-atom Ar-Kr clusters. These values were obtained by smoothing and interpolating the J-walking data shown in Figs. 7 and 8. The uncertainty estimates are averages of single standard deviations of the points near the peaks.

	Mixing Anomaly Peak		Solid-liquid Transition Peak	
	$T_{\text{peak}}$ (K)	$\langle C_V^* \rangle_{\text{peak}}$	$T_{\text{peak}}$ (K)	$\langle C_V^* \rangle_{\text{peak}}$
Ar <sub>13</sub>			34.05 $\pm$ 0.06	118.5 $\pm$ 0.6
Ar <sub>12</sub> Kr			34.41 $\pm$ 0.04	120.6 $\pm$ 0.6
Ar <sub>11</sub> Kr <sub>2</sub>			34.94 $\pm$ 0.10	122.6 $\pm$ 0.5
Ar <sub>10</sub> Kr <sub>3</sub>	2.74 $\pm$ 0.08	38.4 $\pm$ 0.2	35.47 $\pm$ 0.10	123.6 $\pm$ 0.7
Ar <sub>9</sub> Kr <sub>4</sub>	3.41 $\pm$ 0.08	38.9 $\pm$ 0.1	35.86 $\pm$ 0.03	124.1 $\pm$ 0.8
Ar <sub>8</sub> Kr <sub>5</sub>	4.38 $\pm$ 0.10	38.9 $\pm$ 0.1	36.44 $\pm$ 0.18	123.8 $\pm$ 1.2
Ar <sub>7</sub> Kr <sub>6</sub>	3.30 $\pm$ 0.03	39.5 $\pm$ 0.1	37.05 $\pm$ 0.04	122.5 $\pm$ 0.9
Ar <sub>6</sub> Kr <sub>7</sub>	4.14 $\pm$ 0.10	38.9 $\pm$ 0.1	37.63 $\pm$ 0.10	119.9 $\pm$ 0.7
Ar <sub>5</sub> Kr <sub>8</sub>	3.82 $\pm$ 0.23	38.5 $\pm$ 0.2	38.60 $\pm$ 0.06	115.8 $\pm$ 0.9
Ar <sub>4</sub> Kr <sub>9</sub>	3.40 $\pm$ 0.18	38.0 $\pm$ 0.1	39.87 $\pm$ 0.09	112.1 $\pm$ 0.7
Ar <sub>3</sub> Kr <sub>10</sub>			41.30 $\pm$ 0.12	110.2 $\pm$ 0.6
Ar <sub>2</sub> Kr <sub>11</sub>			43.17 $\pm$ 0.09	111.0 $\pm$ 0.6
ArKr <sub>12</sub>	18.71 $\pm$ 0.15	48.6 $\pm$ 0.3	44.86 $\pm$ 0.06	113.6 $\pm$ 0.4
Kr <sub>13</sub>			46.77 $\pm$ 0.09	118.0 $\pm$ 0.6

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